Electronic structure of strongly correlated electron systems 8

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UBC April 2009
On to real materials:
We need to treat

- multi band approaches
- crystal and ligand field splittings
- Hund’s rules and high spin vs low spin states
- orbital degeneracies and orbital ordering
- superexchange interactions, their dependence on structure and orbital occupation
- interplay between spin, charge, orbital and lattice degrees of freedom
New materials and devices

- High Tc superconductors
- Collassal magneto resistance materials
- Multiferroics
- Spintronics and orbitronics
- Surfaces, interfaces, heterostructures of strongly correlated systems
Need multiband/orbital models to describe TM compounds

However numerous studies have shown that this can sometimes be reduced to an effective single band Hubbard model at least for highTc’s BUT ONLY FOR LOW ENERGY EXCITATIONS $E<0.5\text{eV}$
Correlated materials have a wide diversity of properties

Take for example only the transition metal oxides

- **Metals**: CrO2, Fe3O4 T>120K
- **Insulators**: Cr2O3, SrTiO3, CoO
- **Semiconductors**: Cu2O
- **Semiconductor – metal**: VO2, V2O3, Ti4O7
- **Superconductors**: La(Sr)2CuO4, LiTiO4
- **Piezo and Ferroelectric**: BaTiO3
- **Catalysts**: Fe, Co, Ni Oxides
- **Ferro and Ferri magnets**: CrO2, gammaFe2O3
- **Antiferromagnets**: alfa Fe2O3, MnO, NiO ---

Properties depend in detail on composition and structure
As examples we concentrate on 3d Transition metal Oxides. Although 4d’s are also of interest; discussion in first lectures.
Phase Diagram of $La_{1-x}Ca_x MnO_3$

Uehara, Kim and Cheong

R: Rombohedral
O: Orthorhombic (Jahn-Teller distorted)
O*: Orthorhombic (Octahedron rotated)
CAF canted anti ferromagnet
FI ferromagnetic insulator
FM ferromagnetic metal
CO charge ordered
AF antiferromagnetic
Model for Charge, Spin and Orbital Correlations in Manganites

Mn$^{4+}$, d3, $S=3/2$, No quadrupole; Mn$^{3+}$, $S=2$, orbital degeneracy

Mizokawa et al (2001)
Ordering in strongly correlated systems

Stripes in Nd-LSCO

rivers of Charge—Antiferro/Antiphase

\[ \Delta Q < 0.5 \text{ e} \]

Quadrupole moment ordering

\[ \Delta Q_C \sim 1 \text{ e} \]

\[ \Delta Q_0 \sim 0 \]

Charge inhomogeneity in Bi2212

\[ \Delta Q \sim 0.1 \text{ e} \]

Pan, Nature, 413, 282 (2001);
Ti7 Compounds - quite ionic

Cohesive energy → Madelung
+ Anion (np) ↔ Cation (4s, 4p)
hybridization

example valence

\[ 2^n \text{ (don’t exist, or rare)} \]

\[ \begin{array}{llllllll}
\text{Cu}^0 & (1t) & 2^2 & 2^2 & 2^4 & 2^2 & 2^4 & 2^2 & 2^2 \\
\text{Cu}^+ & (2t) & 2^2 & 2^2 & 2^4 & 2^2 & 2^4 & 2^2 & 2^2 \\
\text{Fe}^2+ & (3t) & 2^2 & 2^2 & 2^4 & 2^2 & 2^4 & 2^2 & 2^2 \\
\text{Ti}^2+ & (4t) & 2^2 & 2^2 & 2^4 & 2^2 & 2^4 & 2^2 & 2^2 \\
\end{array} \]

Once we realize that there is
strong anion (np) - Cation (4s, 4p)
hybridization, we often
neglect it and replace
anion (np) orbitals with
effective orbitals
Anion (np) bands quite broad!!
NiCl₂ (non-magnetic)

Ionic Ni³⁺ (d⁶) (³Aₑ) Hund's rule
Often predicted to be small gaped insulators, NiO, La$_2$CuO$_4$, CoO and non magnetic de Boer - Verwey - 1937 showed that these are large gap insulators. They also are magnetically ordered.

As we go from F, Cl, Br, I or O, S, Se, Te we expect the np band to move towards EF and can cross 3d band??!!
Cooperative Behaviour of Electrons

Instead of Bloch \rightarrow Ionic Ansatz

Absolute minimum basis set !!

Stay at home principle
(Herring)

\[ \begin{align*}
\text{Mott-Hubbard } U & \quad \text{Hund's Rule} \\
U = (E(d^{n+1}) - E(d^n)) + (E(d^{n-1}) - E(d^n)) & \quad \text{Affinity} + \text{Ionization} \\
& = 16 \text{eV for free ion} \\
\Delta = E(d^{n+1}L) - E(d^n) & \quad \text{Charge Transfer} \\
& = E(d^n) + E_t(p^6) + 2E_{\text{Hubbard}} \\
& \quad \text{or}(V_L) + V_n(r_m) \\
\text{In the solid we have large correction terms!! (Screening)}
\end{align*} \]
To calculate the gap we calculate the ground state of the system with $n, n-1,$ and $n+1$ d electrons.

Then the gap is

$$E(\text{Gap}) = E(n-1) + E(n+1) - 2E(n)$$
3 most frequently used methods

• Anderson like impurity in a semiconducting host consisting of full O 2p bands and empty TM 4s bands including all multiplets

Developed for oxides in early 1980’s, Zaanen, Kotani, Gunnarson,------

• Cluster exact diagonalization methods. O cluster of the correct symmetry with TM in the center. Again include all multiplets crystal fields etc

Developed for oxides in early 1980’s Fujimori, Thole, Eskes, ------

General soft ware by de Groot, Tanaka

• Dynamic Mean Field methods, CDMFT, DCA which to date do not include multiplets

Developed in the late 1990’s: Kotliar, George, Vollhart---
Schematic Calculation of $E_{gap}$

$n-1$ (UPS)  $n$ (neutral)  $n+1$ (BIS)

Notice inversion! $U > \Delta$

$E_{gap} = E_I + E_A$
Will treat a specific case later

\[ E_{\text{gap}} = \Delta + 2S^n - S^{n-1} - S^{n+1} \]

\[ \Delta = \text{Charge Transfer energy} = E(d^n) \rightarrow E(d^{n+1} \downarrow) \]

\( \downarrow \) denotes a hole in anion(np)

\[ \Delta = \varepsilon_d - \varepsilon_L \] [with \( \varepsilon_d \) the electron addition energy \( d^n \rightarrow d^{n+1} \uparrow \)]

Using impurity theory

Gunnarson - Schönhammer PRL 50, 604
PRB 28, 4315 (83); 31, 4816 (85)

We can get \( S^n \)

\[ S^n = 2 \int_{-\frac{w}{2}}^{\frac{w}{2}} \frac{T^{2}e^{(c)}}{S^{n} - \Delta - \varepsilon - 2\varepsilon(S^{n-1} - \Delta - u - \varepsilon)} \, d\varepsilon \]

\[ M(2) = \int_{-\frac{w}{2}}^{\frac{w}{2}} \frac{T^{2}e^{(c)}}{2 - \varepsilon} \, d\varepsilon \] [Take a hemispherical band for (np)]
Get used by fitting PES/IPES

NiO \left( \text{Ni}^{2+} 3d^8, \text{O}^{2-} 2p^6 \right)
For divalent cations
Classification scheme according to ZSA

Zaanen 1985

Veel deltjes theorie

CuI₂ (not stable)

\(E_{\text{gap}} \propto \Delta\)

\(\Delta = U\)

\(E_{\text{gap}} = 0.5T\)

\(E_{\text{gap}} = 0\)

\(D\) (metal)

\(C\) (metal)

\(T_{2g}^0\)

\(T_{2g}^0V_{4}\)
Figure 9.4. The charge-transfer energy ($\Delta_{\text{Cr}}$, solid line) and $U_{\text{eff}}$ ($U_{\text{Cr}}$, dashed line) including the electrostatic crystal field contributions compared to the quasi-atomic $\bar{U}$ and $\bar{U}$ (dashed line, resp. dotted line).
More General Models

Multi-band, Multiplets

Trans. Met Comp. 3d\textsuperscript{n} (orbital deg.)
(Rare Earth)
(Hunds rule)
(MultipletS)
(Crystal fields)

other bands $O_{xp}$

\[ \downarrow \downarrow + Hybridization \] (Covalency)

\[ \lambda = \sum \frac{m}{n} \epsilon_{d_n} \epsilon_{p_n} + \sum \frac{m}{n} \epsilon_{p_{m+n}} p_n p_n + \sum \frac{m}{n} \epsilon_{d_{m+n}} (d_{m+n}^+ p_n + \ldots) \]

\[ + \sum \frac{m}{n} \epsilon_{p_{m+n}} p_n p_n + \sum \epsilon_{d_{m+n}} (d_{m+n}^+ p_n + \ldots) \]

\[ + \sum \epsilon_{d_{m+n}} U_{dd}(nn'nn''mm') d_{m+n}^+ d_{m+n} d_{m+n} d_{m+n} \]

\[ \text{MultipletS.} \]

\(\text{Neglect in first instance}\)

Ok if the anion (xp) band is full or nearly so.
However don't forget $U_{pp} \approx 6\text{eV}$
Two new complications

• d(n) multiplets determined by Slater atomic integrals or Racah parameters A,B,C for d electrons. These determine Hund’s rules and magnetic moments

• d-O(2p) hybridization (d-p hoping int.) and the o(p)-o(p) hoping (o 2p band width) determine crystal field splitting, superexchange, super transferred hyperfine fields etc.
See Harrison’s book on tight Binding band theory. Harrison Derives hoping parameters in terms Of interatomic distances, orbital radii,
• We usually take \( U(\text{pp}) = 0 \) although it is about 5 eV as Measured with Auger but the O 2p band is usually full or nearly full.

\[
U_{dd} = E_z(d^n) - E_A(d^n) \quad \text{[Hands Rule]}
\]

\( U_{dd} \) contains \( F^0, F^3, F^4 \)

and also some crystal field.

For TM compounds use Racah parameters instead of Slater:

\[
A = F_0 - 49F_4 \quad B = F - 5F_4 \quad C = 35F_4
\]

[Again New convention \( F_4 \).]

\[
F_2 = \frac{1}{49} F^3, \quad F_4 = \frac{1}{448} F^2, \quad F_6 = F^4
\]

\( B = C \) from Optical Spectra of free ions [or from solid]

\( \Rightarrow \) Moore's Tables
Reduction of coulomb and exchange in solids

- Recall that U or F0 is strongly reduced in the solid. This is the monopole coulomb integral describing the reduction of interaction of two charges on the same atom.
- However the other integrals F2 and F4 and G’s do not involve changes of charge but simply changes of the orbital occupations of the electrons so these are not or hardly reduced in solids. The surroundings does not care much if local eg the spin is 1 or zero.
- This makes the multiplet structure all the more important!!!!!
Hunds Rule

First the Physics

Spin parallel electrons must be in different spatial orbitals i.e. \( m_l \) must be different if they are in the same shell i.e. \( l_1 = l_2 \Rightarrow \) Pauli

\[ \Rightarrow \]

Lower Coulomb interaction

\[ \Rightarrow \]

Hunds 1st Rule: Max. \( S \)

Large \( m_s \) values means lots of lobes. Two electrons with different \( m_s \) have lower Coulomb repulsion because they can avoid each other. The larger \( m_s \) the better.

Hunds 2nd Rule: \( \text{Max. } l \)
A little more formal

From Slater Quantum Theory of Atoms and Molecules, chapter 13 + appendix 20

1. electron wave function

\[ \psi_{nlm} = \frac{(-1)^l}{\sqrt{4\pi}} \sqrt{\frac{(2l+1)(2l-1m^2)}{(2l^2 - 1)}} \frac{R_n(r)}{r} P_l^{m_l}(\cos \theta) e^{im\phi} \]

\[ \rho_{ij} = \sum_j f_{ij} + \sum_{\text{pairs } ij} q_{ij} \]

One electron: \(-\frac{\nabla^2}{2r} - \frac{2}{r}\)

\[ q_{ij} = \frac{2}{r_{ij}} \rightarrow \text{Multiples} \rightarrow \text{Hund's rule} \]

We need to calculate \( \langle ij | q | r \rangle \) where \( i, j, r, s \)

Label the q.n.'s of occupied states

And sum over all pairs \( i, j, r \) that are occupied in \( \Psi \)
Two Types of Integrals
\[ \langle i | q | l | i j \rangle \] and \[ \langle i j | q | l | i j \rangle \]

For 2 electrons in same shell
\[ \langle i j | q | l | i j \rangle = \sum_{k=0}^{\infty} a^k (l, m_l; l, m_l) F^k (n, l, \ell; n, l, \ell) \]

\[ F^k = R^k (i j; i j) \rightarrow \text{Direct Coulomb} \]

\[ \langle i j | q | l | i j \rangle = \sum_{l, m_l} b^k (l, m_l) G^k (l, m_l) \]

\[ b^k (l, m_l; l, m_l) = \left[ C^k (l, m_l) \right]^2 \]

\[ C^k (n, l, \ell; n, l, \ell) = \sum_{l, m_l} R^k (r_i) R^k (r_j) R (r_i) R (r_j) 2 \frac{r_i^2 r_j^2}{r_i r_j} \]
\[
\frac{1}{V_{12}} = \sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-1m)!}{(k+1m)!} \frac{v_{k}^{k}}{v_{k}^{m+1}} P_{k}(\cos \phi_{1}) P_{l}(\cos \phi_{2})\]

\[
x \lim (\phi_{1} - \phi_{2})^{1}
\]

\[
\langle i_{\phi_{1}} g_{1} r_{2} \rangle = \int \int \psi_{i}^{*}(r_{1}) \psi_{l}(r_{2}) \frac{1}{1_{r_{1}} 1_{r_{2}}} \psi_{i}(r_{1}) \psi_{l}(r_{2}) \, dr_{1} \, dr_{2}
\]

\[
\therefore \quad 1_{r_{1}} = 1_{r_{2}} \quad 1_{r_{1}} = 1_{r_{2}}
\]

\[
\sum_{k=0}^{\infty} \sum_{m=-k}^{k} \frac{(k-1m)!}{(k+1m)!} (-1)^{m} \frac{m_{2}^{2} + m_{3}^{2} + m_{1}^{2} + m_{4}^{2}}{(l_{e} + \frac{1}{2}) l_{e} - (m_{2}^{2})^{1}}
\]

\[
x \int \int \frac{R_{i}^{*}(r_{1}) R_{l}(r_{2}) R_{i}^{*}(r_{1}) R_{l}(r_{2})}{v_{k}^{m+1}} \frac{2r_{1}^{k}}{v_{k}^{2}} r_{1}^{2} r_{2}^{2} \, dr_{1} \, dr_{2}
\]

\[
x \int \int P_{i}^{m}(\cos \phi_{1}) P_{l}^{m}(\cos \phi_{2}) \frac{P_{i}^{m}(\cos \phi_{1})}{P_{l}^{m}(\cos \phi_{2})} \sin \phi_{1} \, d\phi_{1}
\]

\[
x \int \int P_{i}^{m}(\cos \phi_{1}) P_{l}^{m}(\cos \phi_{2}) \frac{P_{i}^{m}(\cos \phi_{1})}{P_{l}^{m}(\cos \phi_{2})} \sin \phi_{2} \, d\phi_{2}
\]

\[
x \int \int e^{i-(m_{2}^{2} + m_{3}^{2} + m_{1}^{2})/2} \, d\phi_{1} \, x \int \int e^{i-(m_{2}^{2} + m_{3}^{2} + m_{1}^{2})/2} \, d\phi_{2}
\]
From orthogonality \( \phi \)

\[ m = m_x - m_y = -m_y + m_z \]
\[ m_z + m_y = m_x + m_z \] (Consrv. 17)

So we use

\[ c^k(l_m; l'_m) = (-1)^{(m+l_m+l'_m+m'(l_m)+m'(l'_m)+(m_mkee_m')l/2)} \]
\[ \times \sqrt{\frac{(k + l_m + l'_m)!}{(k + l'_m)!}} \sqrt{\frac{(2k+1)(l_m)_m!}{(l_m)_m!}} \]
\[ \times \frac{1}{2} \int \frac{1}{E^l_{l_m}} \frac{1}{E^{l'_m}_{l'_m}} \frac{1}{E^{l_m-m'_m}_{l_m-m'_m}} \]

Tabulated \rightarrow Appendix 20

\[ \langle q_1 q_2 \rangle = \langle m_{x_1} m_{x_2} \rangle \langle m_{y_1} m_{y_2} \rangle \langle m_{y_1} + m_{y_2} \rangle \langle m_{z_1} + m_{z_2} \rangle \]
\[ \times \sum_{k=0}^{l} c^k(l_m; l'_m) c^k(l_{m_1} + l_{m_2}; l_{m_1} + l_{m_2}) \]

Highest possible value of \( k = l + l' \)

i.e. \( l_i + l_{x_2} \) or \( l_i + l_{z_2} \)
Hund's 3rd rule

< half filled \( J = L - S \)

> half filled \( J = L + S \)

\[ \text{Spin - Orbit Coupling} \]

\[ H' = \sum \frac{1}{2m^2c^2} (\vec{\nabla} \cdot \vec{r}_j \times \vec{p}_j) \cdot \vec{S}_j \]

For 1 electron \( J = L - S \) is lowest

i.e. for d electron \( J = \frac{3}{2} \)

For 1 hole \( \vec{J}_{\text{hole}} = \vec{L} + \vec{S} \)

i.e. for \( d^9 \) \( J = \frac{5}{2} \) (lowest)
Spin-orbit results in magnetic anisotropy
- $g$ factor different from 2
- Orbital contribution to magnetic moment
- $D \cdot \hat{5}_1 \times \hat{5}_2$ like interactions
Multiplet Structure

Free atom

\[ E(n, l, s, d) = n I + \frac{1}{2} n(n-1) U_{av} + U(n, l, s, d) \]

\[ U_{av}^{dd} = F^0 - \frac{2}{63} (F^2 + F^4) = F^0 - \frac{2l}{72+1} J(d, d) \]

\[ J(d, d) = \frac{1}{14} \left( F^2 + F^4 \right) \]

\[ U_{av}^{ff} = F^0 - \frac{2e}{42+1} J(ff) \]

\[ J(ff) = \frac{1}{6435} \left( 298 F^2 + 195 F^4 + 250 F^6 \right) \]

\[ C(dd) = \frac{1}{14} \left( \frac{9}{7} F^2 - \frac{5}{7} F^4 \right) \]

\[ C(ff) = \frac{1}{6435} \left( 286 F^2 + 280 F^4 + 1750 F^6 \right) \]

\[ E(n, HR) = \delta_{\text{c}}(n) I + \alpha_{\text{c}}(n) F^0 + \delta_{\text{c}}(n) J + \alpha_{\text{c}}(n) C \]

\[ U_{av}^{ff} = E(n+1, HR) + E(n-1, HR) - 2E(n, HR) \]

\[ \text{C are not screened} \]
Coulomb integrals

\[ U = F_2^0 = 1.0 \text{ eV} \]
\[ F_2 = 8.94 \text{ eV} \]
\[ F_4 = 5.62 \text{ eV} \]

For \( 17n (d^{15}) S = \frac{5}{2} \)

\[ 3(d^{n+1}) + 3(d^{n-1}) - 2E(d^0) = U + 4 \cdot J_{\text{Hahn}} \]

\[ J_{\text{Hahn}} = \frac{1}{14} (F_2^2 + F_4^2) \approx \text{1 eV per Spin pair} \]
Table 2.1. Parameters determining the energies of the Hund's Rule ground states in LS coupling for all d occupations and the expression for the d-d gap for those occupations.

<table>
<thead>
<tr>
<th>state</th>
<th>$\alpha_1$</th>
<th>$\alpha_{F0}$</th>
<th>$\alpha_J$</th>
<th>$\alpha_C$</th>
<th>$U^{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^0(1S)$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$d^1(^2D)$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$d^2(^3F)$</td>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$F^0_{0-J-C}$.</td>
</tr>
<tr>
<td>$d^3(^4F)$</td>
<td>3</td>
<td>3</td>
<td>-3</td>
<td>-1</td>
<td>$F^0_{0-J+C}$.</td>
</tr>
<tr>
<td>$d^4(^5D)$</td>
<td>4</td>
<td>6</td>
<td>-6</td>
<td>0</td>
<td>$F^0_{0-J-C}$.</td>
</tr>
<tr>
<td>$d^5(^6S)$</td>
<td>5</td>
<td>10</td>
<td>-10</td>
<td>0</td>
<td>$F^0_{0-J-C}$.</td>
</tr>
<tr>
<td>$d^6(^5D)$</td>
<td>6</td>
<td>15</td>
<td>-10</td>
<td>0</td>
<td>$F^0_{0-J-C}$.</td>
</tr>
<tr>
<td>$d^7(^4F)$</td>
<td>7</td>
<td>21</td>
<td>-11</td>
<td>-1</td>
<td>$F^0_{0-J+C}$.</td>
</tr>
<tr>
<td>$d^8(^3F)$</td>
<td>8</td>
<td>28</td>
<td>-13</td>
<td>-1</td>
<td>$F^0_{0-J+C}$.</td>
</tr>
<tr>
<td>$d^9(^2D)$</td>
<td>9</td>
<td>36</td>
<td>-16</td>
<td>0</td>
<td>$F^0_{0-J-C}$.</td>
</tr>
<tr>
<td>$d^{10}(1S)$</td>
<td>10</td>
<td>45</td>
<td>-20</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

For $d^5$:

\[
U = F^0_{0-J-C} + 4J
\]

For $d^{10}$:

\[
U = F^0_{0-J-C}
\]

In $\text{LaMnO}_3$:
Crystal & ligand fields

\[ \psi_d \text{ (Free ion)} \sim \psi_{2m}(\theta, \phi) \to \rho_2(\text{cos} \theta) e^{im\phi} \]

\[ l = 2, \quad m_2 = \pm 2 \pm 10 \]

\[ j = l + \frac{5}{2} \text{ or } l - \frac{5}{2} \text{ (Hund's rule)} \]

Spin orbit coupling \( \sim j l \cdot \frac{5}{2} \) is \( \sim 30 \text{ meV} \) often \( \ll \) crystal field

Often orbital moment is quenched

Construct real orbitals

4. Octahedral symmetry, Octahedral Coordination

Diagram showing octahedral coordination with ligands at the vertices.
Angular distribution of “real” d orbitals
in $O_{h}$ symmetry 2 kinds of d-orbitals

d$_{xy}$, d$_{xz}$, d$_{yz}$ → $t_{2g}$

d$_{x^2-y^2}$, d$_{3z^2-r^2}$ → $e_g$

$e_d_{xy} = \frac{1}{\sqrt{2}} \left( [22-2] - 2 \frac{\epsilon_2}{\epsilon_2} \right) \rightarrow (\ell_2 = 0)$

$\text{d}_{3z^2-r^2} = [20] \quad (\ell_2 = 0)$

$\text{d}_{x^2-y^2} = \frac{1}{\sqrt{2}} \left( [22-2] + [22] \right) \quad (\ell_2 = 0)$

Spin-orbit coupling does not split the $e_g$'s to first order

i.e. $\ell_2 = 0$ does not mix with $\ell_2 = \pm 2$

via spin-orbit

$e_g$'s can split via spin-orbit also $\ell$-$s$ causes $e_y$-$e_g$ mixing
Crystal and ligand field splittings

1) Point charge contribution

\[ V = \sum_{nm} n^m A_n^m \rho_{nm}^m (\cos \theta) e^{im\phi} \]

\[ \langle d_z^2 | V | d_z^2 \rangle = \Delta E \]

Octahedron - Cubic - \(O_h\)

\( \zeta = x^2-y^2, z^2-r^2 \) (eq)

\( \zeta = xy, xz, yz \) (eq)

\( n = 0, \frac{1}{2} \) for \( \Delta E \neq 0 \)

\( \Delta E = \langle d_z^2 | V | d_z^2 \rangle \times \text{angular part} \)

\[ V = A_0 \rho_{1/2} \left[ \rho_{1/2} (\cos \theta) - (\zeta)^{1/2} (\rho_{1/2} e^{im\phi} + \rho_{1/2} e^{-im\phi}) \right] \]

2) Overlap contribution

Often about 0.5 eV

In Oh symmetry

Angular integrals
Are different for t2g and eg
Eg-O2p hoping is 2 times as large as T2g-O-2p hoping

Often about 1-2eV
In Oxides
The coulomb interactions in terms of real space d orbitals


Coulomb (J) and exchange (K)

\[ J(x_2, y_2) = \int \langle x_2^* \langle 1 \rangle y_2^* \langle 2 \rangle \frac{1}{r_{12}} \rangle x_{2\langle 1 \rangle} y_{2\langle 2 \rangle} \, d\tau \]

\[ K(x_2, y_2) = \int \langle x_2^* \langle 1 \rangle y_2^* \langle 2 \rangle \frac{1}{r_{12}} \rangle y_{2\langle 1 \rangle} x_{2\langle 2 \rangle} \, d\tau \]
Table 4-5. Coulomb Integrals (J) and Exchange Integrals (K) of the
Set \( t_{2g}(xz,yz,xy) \) and \( e_g(x^2 - y^2, z^2) \) (Ref. 19)

\[
\begin{align*}
J(z^2, z^2) &= J(x^2 - y^2, x^2 - y^2) = J(xy, xy) = J(xz, xz) = J(yz, yz) \\
&= F_0 + 4F_2 + 36F_4 \\
J(x^2 - y^2, xz) &= J(x^2 - y^2, yz) = J(xy, yz) = J(xy, xz) \\
&= 2F_0 - 2F_2 - 4F_4 \\
J(z^2, xz) &= J(z^2, yz) = F_0 + 2F_2 - 24F_4 \\
J(z^2, xy) &= J(x^2, x^2 - y^2) = F_0 - 4F_2 + 6F_4 \\
J(x^2 - y^2, xy) &= F_0 + 4F_2 - 34F_4 \\
K(xy, yz) &= K(xy, xz) = K(xz, yz) = K(x^2 - y^2, xz) = K(x^2 - y^2, yz) \\
&= 3F_2 + 20F_4 \\
K(x^2, x^2 - y^2) &= K(z^2, xy) = 4F_2 + 15F_4 \\
K(z^2, xz) &= K(x^2, yz) = F_2 + 30F_4 \\
K(x^2 - y^2, xy) &= 35F_4
\end{align*}
\]

Table 4-6. Values of the Matrix Elements \((ab|1/r_{12}|cd)\) Different
From Zero

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<tbody>
<tr>
<td>((xz))</td>
<td>((z^2))</td>
<td>((xz))</td>
<td>((x^2 - y^2))</td>
<td>(-2\sqrt{3} F_2 + 10 \sqrt{3} F_4)</td>
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<tr>
<td>((yz))</td>
<td>((z^2))</td>
<td>((yz))</td>
<td>((x^2 - y^2))</td>
<td>(2 \sqrt{3} F_2 - 10 \sqrt{3} F_4)</td>
</tr>
<tr>
<td>((xz))</td>
<td>((xz))</td>
<td>((z^2))</td>
<td>((x^2 - y^2))</td>
<td>(\sqrt{3} F_2 - 5 \sqrt{3} F_4)</td>
</tr>
<tr>
<td>((yz))</td>
<td>((yz))</td>
<td>((xz))</td>
<td>((yz))</td>
<td>(- \sqrt{3} F_2 + 5 \sqrt{3} F_4)</td>
</tr>
<tr>
<td>((x^2))</td>
<td>((xy))</td>
<td>((xz))</td>
<td>((yz))</td>
<td>(\sqrt{3} F_2 - 5 \sqrt{3} F_4)</td>
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<tr>
<td>((z^2))</td>
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<td>((yz))</td>
<td>((xz))</td>
<td>(\sqrt{3} F_2 - 5 \sqrt{3} F_4)</td>
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<tr>
<td>((z^2))</td>
<td>((xz))</td>
<td>((xy))</td>
<td>((yz))</td>
<td>(2 \sqrt{3} F_2 - 10 \sqrt{3} F_4)</td>
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<tr>
<td>((x^2 - y^2))</td>
<td>((xy))</td>
<td>((xz))</td>
<td>((yz))</td>
<td>(3F_2 - 15F_4)</td>
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<tr>
<td>((x^2 - y^2))</td>
<td>((xy))</td>
<td>((yz))</td>
<td>((xz))</td>
<td>(-3F_2 + 15F_4)</td>
</tr>
</tbody>
</table>
Interplay between crystal Fields and multiplet structure
Optical for NiO

Use Auger theory (Saoltsy PRl 39, 504 (1973))

(d^8 is the same as 2 holes in d^10)

Dyson \( G = g + g \mathcal{H} G \)

before \( \mathcal{H} = \frac{\epsilon}{\hbar^2} v_H (c_i^+ d + h.c) \)

Now take \( \mathcal{H} = \sum_{ij} U(ij\lambda\mu) d_i^+ d_j d_\lambda^+ d_\mu \)

Simple example is imp. state

\[
\langle 00^0 \rangle = \langle 00^0 \rangle + \langle 00^0 \rangle U \langle 00^0 \rangle
\]

Kanamori: average T-matrix is exact!

\[
\langle 00^0 \rangle = \frac{\langle 00^0 \rangle}{1 - U \langle 00^0 \rangle}
\]

\[\langle 00^0 \rangle = \frac{1}{2U} \langle 00^0 \rangle \]

are more complicated

IR in \( O_h \) spanned by 2 d holes

of \( Eg \) or \( T_{2g} \) symmetry are

\[3 A_{2g}, \ 'E_g', 'T_{2g}', 'T_{1g}', 3 T_{2g}, 3 T_{1g}, 'A_{1g}' \]
Fig. 2. Absorption spectrum of NiO at 300 K, 77 K. Dashed lines are interpolations.
The whole eigenstates starting from \( d^0 \) in an Op band would give us the \( d \)-excitations. For \( U = 0 \) the possible states are \( |ij\rangle = |e_{ij}^\uparrow\rangle, |e_{ij}^\downarrow\rangle, \mid\rangle \). IR \rightarrow \text{Irreducible reps. of the Oh point group}

\[
G_{ij}^{e_{ij}^\uparrow} (\text{IR}, z) = G_{ij}^{e_{ij}^\downarrow} (\text{IR}, z) S_{ij}^{ee} S_{ij}^{ee} +
\sum_{mn} G_{ij}^{e_{ij}^\uparrow} (\text{IR}, z) U_{ij}^{mn} G_{mn}^{e_{ij}^\downarrow} (\text{IR}, z)
\]

\( U_{ij}^{mn} \) are tabulated (Griffith). Possible two-particle states are \( ^3\text{A}_2, ^3\text{T}_2, ^3\text{T}_1 \) \{single's\}, \( ^1\text{E}, ^1\text{A}_1, ^3\text{T}_1, ^1\text{T}_2 \) \{2 fold\}

\[
G_{ij}^{e_{ij}^\uparrow} = g_j^{\uparrow} \otimes g_j^{\uparrow} = 3c
\]

\[
q_{ij}^{(2)} = \frac{1}{2 - \sqrt{1} (2 - \alpha - \mu)} \quad q_j^{(1)} = \frac{1}{2 - \sqrt{1} (2 - \alpha - \mu)}
\]
Table 7.1. Fitting parameters and energies of d-d transitions (all in eV) several Ni-compounds obtained from the impurity calculation. I in parenthesis are the experimental energies (see refs. 16, 17. Also included are the predicted ground state d-occupations (<n

<table>
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<tr>
<th></th>
<th>$\Delta$</th>
<th>$V_e$</th>
<th>$V_t$</th>
<th>10 $Dq$</th>
<th>$^{3}T_2$</th>
<th>$^{1}E$</th>
<th>$^{3}T_1$</th>
<th>$^{1}A_1$</th>
<th>$^{1}T_2$</th>
<th>$^{3}T_1$</th>
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<td>0.8</td>
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<td>1.89</td>
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<td>3.22</td>
<td>3.36</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(1.13)</td>
<td>(1.75)</td>
<td>(1.95)</td>
<td>(2.75)</td>
<td>(2.95)</td>
<td>(3.25)</td>
<td>(3.52)</td>
<td></td>
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<td>1.4</td>
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<td>0.65</td>
<td>0.96</td>
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<td>1.60</td>
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<td>2.70</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.95)</td>
<td>(1.69)</td>
<td>(~1.52)</td>
<td>(2.50)</td>
<td>(2.80)</td>
<td>(2.80)</td>
<td></td>
<td></td>
</tr>
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<td>NiBr$_2$</td>
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<td>0.8</td>
<td>0.58</td>
<td>0.95</td>
<td>1.55</td>
<td>1.55</td>
<td>2.30</td>
<td>2.52</td>
<td>2.75</td>
<td>2.90</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.94)</td>
<td>(~1.58)</td>
<td>(~1.58)</td>
<td>(2.06)</td>
<td>(2.57)</td>
<td>(2.57)</td>
<td></td>
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<tr>
<td>NiI$_2$</td>
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<td>0.93</td>
<td>1.38</td>
<td>1.52</td>
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<td></td>
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<td></td>
<td></td>
<td>(~0.95)</td>
<td>(1.38)</td>
<td>(1.51)</td>
<td></td>
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<td></td>
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</table>
Estimates of $U$ or $F^0$

For $^{17}\text{Mn}$ in Aq, we found $F^0 \approx 1\text{eV}$

Atomic $F^0$ from spectroscopy $\approx 15\text{eV}$

Reduction of $U$ via backflow of charge to the $4s\ 4p$ local orbitals upon removal or addition of a $d$ electron

Herring used $2d^n s^2 \rightarrow d^{n+1}d^{n-1}$

$\Delta E$ for $^{17}\text{Mn}$ is about $1\text{eV}$ (see Table 1 of Reference)

Such changes in the $4s\ 4p$ occupation will strongly reduce $U$ and is the main reason for small $F^0$'s in metals

In compounds like oxides we can reduce $U$ by the polarizability of $O^{2-}$ ($\alpha = 3\text{A}^2$)

This reduces $U \rightarrow U - 2E_p$, $\approx U - 6\text{eV}$
Also use $4S, 4p$ and the strong $O_{2p} \rightarrow 4s, p$ hybridization.

The $3d - 4s$ Coulomb will push up the $4s$ energy relative to $O_{2p}$ for $d^n \rightarrow d^{n+1}$ and will lower $4s$ for $d^n \rightarrow d^{n-1}$.

Relevant terms for this are $E_{ap,4s} = \langle O_{2p} | d | 1d4s \rangle$ $E_{ap,4s}$ and $U_{4s,3d}$.

A model is easily worked out.

$U_{4s,3d}$ for $17n \sim 7-9 \text{eV}$

$E_{ap} - E_{4s} \sim 12-15 \text{eV}$

$\sqrt{6} E_{ap,4s} \sim 5 \text{eV}$ (recall each $4s$ mixes with 6 surrounding $O_{2p}$'s and with spin $\uparrow$ and $\downarrow$).
B, C Not Screened → Multiplet's (d^\text{\textsuperscript{n}})

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MnO</th>
<th>FeO</th>
<th>CoO</th>
<th>NiO</th>
<th>CuO</th>
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<tr>
<td>Racah A</td>
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<td>6.5</td>
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<td>B</td>
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<td>0.14</td>
<td>0.13</td>
<td>0.15</td>
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<tr>
<td>C</td>
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<td>0.54</td>
<td>0.60</td>
<td>0.58</td>
</tr>
<tr>
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<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>pd\pi</td>
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<td>-0.6</td>
<td>-0.6</td>
<td>-0.6</td>
<td>--</td>
</tr>
<tr>
<td>(pp\sigma-pp\pi)</td>
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<td>-0.7</td>
<td>-0.7</td>
<td>-0.7</td>
<td>-1.0</td>
</tr>
<tr>
<td>\Delta</td>
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<td>7.0</td>
<td>5.5</td>
<td>6.2</td>
<td>2.8</td>
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<td>U</td>
<td>A+14B+7C</td>
<td>A-8B</td>
<td>A+B</td>
<td>A+B</td>
<td>A+4B+2C</td>
</tr>
<tr>
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<td>4.5</td>
<td>5.3</td>
<td>6.7</td>
<td>8.3</td>
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<td>3.1</td>
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<td>1.8</td>
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<tr>
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<td>2.5</td>
<td>4.3</td>
<td>1.4</td>
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<td>Int</td>
<td>MH</td>
<td>Int</td>
<td>CT</td>
<td>CT</td>
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<td>6A_{19}</td>
<td>3T_{19}</td>
<td>2E_{g}</td>
<td>1A_{19}</td>
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</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MnO</th>
<th>FeO</th>
<th>CoO</th>
<th>NiO</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO d^8</td>
<td>U = A+B</td>
<td>U = A+B</td>
<td>U = A+B</td>
<td>U = A+5B+4C</td>
<td>U = A-8B</td>
</tr>
<tr>
<td>CoO d^7</td>
<td>U = A+B</td>
<td>U = A+B</td>
<td>U = A+B</td>
<td>U = A+5B+4C</td>
<td>U = A-8B</td>
</tr>
<tr>
<td>FeO d^6</td>
<td>U = A-8B</td>
<td>U = A-8B</td>
<td>U = A-8B</td>
<td>U = A-8B</td>
<td>U = A-14B+7C</td>
</tr>
<tr>
<td>MnO d^5</td>
<td>U = A-8B</td>
<td>U = A-8B</td>
<td>U = A-8B</td>
<td>U = A-8B</td>
<td>U = A-8B</td>
</tr>
</tbody>
</table>

Table 2. Parameters for the different late transition metal monoxides, for MnO, FeO, and NiO see the following chapters. CuO is taken from Eskes et al. [7], who used a similar cluster calculation. All the values are in eV. In the bottom SA stands for Zaanen, Sawatzky, and Allen phase diagram [6], Int is intermediate region, MH is Mott-Hubbard region and CT is charge transfer region. The last line shows the first ionization state symmetry (f.i.s.s.) in O_h and D_{4h} (CuO) symmetry.
Simplified pictures of crystal field and multiplets

\[ d^n \text{ energy levels with } \phi \text{ crystal field and Hund's First rule} \]
\[ \text{i.e. } d-d \text{ Coulomb } F^0 + \frac{1}{14} (F^2R^4) \]
\[ \text{neglect other contributions to multiplet splitting.} \]

This is a good starting picture.
For exact go to Tanaka-Sugano diagrams.
$T_{pd}(eg) = 2 \times T_{pd}(t_{2g})$
High Spin – Low Spin transition very common in Co(3+)(d6), as in LaCoO3, not so common in Fe(2+)(d6) Because of the smaller hybridization with O(2p)

In some cases also the spin is quenched [3d⁶ in O₄]
Mixed valent system could lead to strange effects
Such as spin blockade for charge transport and high
thermoelectric powers

Removing 1 electron from d^6
Could change S by 5/2↑↓

Very heavy QP??

FIG. 8.1. Schematic picture of the electron removal energies (solid lines) and one electron excitation energies (dashed lines) for d^6 and d^5. The left panel represents the free ion and the central panel corresponds to the ion in a weak crystal field, which is further increased in the panel on the right. Note that the exchange splittings of the majority and minority spin states for high spin and low spin are different.
What would happen if $2J_h < 10D_q < 3J_h$

If we remove one electron from d6 we would go from $S=0$ in d6 to $S=5/2$ in d5. The "hole" would carry a spin of $5/2$ as it moves in the d6 lattice.

$LaCoO_3$ is low spin $^{\text{Co}^{3+}}(S=0)$ for $T<100K$

First ionization state is $^{\text{Co}^{4+}}$ high spin $(S=5/2)$

"...First electron removal state cannot be reached by removing 1 electron only $Z=0$!!

$La_{1-x}Sr_xCoO_3$

\[3t^3 3t^3 4t^1 3t^3 3t^3 \]

$s=0, s=0, s=5/2, s=0, s=0, s=0$  

Not possible with one electron terms.

Very heavy quasi particle!
TABLE 8.1. The possible lowest and highest spin states of an 3d ion with n d electrons in a local surrounding of octahedral ($O_h$) or tetrahedral ($D_{4h}$) symmetry. The arrows indicate electron removal or electron addition transitions with $|\Delta S| > \frac{1}{2}$.

<table>
<thead>
<tr>
<th></th>
<th>$d^0$</th>
<th>$d^1$</th>
<th>$d^2$</th>
<th>$d^3$</th>
<th>$d^4$</th>
<th>$d^5$</th>
<th>$d^6$</th>
<th>$d^7$</th>
<th>$d^8$</th>
<th>$d^9$</th>
<th>$d^{10}$</th>
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<td>$O_h$</td>
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<td></td>
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<td></td>
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<td></td>
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<tr>
<td>High</td>
<td>0</td>
<td>1/2</td>
<td>1</td>
<td>3/2</td>
<td>2</td>
<td>5/2</td>
<td>2</td>
<td>3/2</td>
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<tr>
<td>Low</td>
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<td>1/2</td>
<td>1</td>
<td>3/2</td>
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<td>$D_{4h}$</td>
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<tr>
<td>Low</td>
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<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
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<td>1/2</td>
<td>0</td>
<td>1/2</td>
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</table>

TABLE 8.2. The combined crystal and ligand field splitting ($10Dq$) required for a transition from high spin to low spin.

<table>
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<tr>
<th></th>
<th>$d^2$</th>
<th>$d^3$</th>
<th>$d^4$</th>
<th>$d^5$</th>
<th>$d^6$</th>
<th>$d^7$</th>
<th>$d^8$</th>
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<tr>
<td>$10Dq$ (eV)</td>
<td>-</td>
<td>-</td>
<td>2.36</td>
<td>2.67</td>
<td>1.74</td>
<td>1.98</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A window of 1 eV!!
FIG. 4 (color online). The scheme showing the processes of electron (a), (b) and hole (c) hopping on the background of the HS and LS Co$^{3+}$ (a) and LS Co$^{3+}$ (b), (c). (b) illustrates the phenomenon of a spin blockade. (a) applies to the high-temperature metallic phase of HoBaCo$_2$O$_{4.5}$, whereas (c) corresponds to the processes available at the low temperature insulating phase.
Goodenough Kanamori Anderson rules

If the charge transfer energy gets small we have to Modify the superexchange theory

\[
\text{Super exchange} \\
\text{Cu}^{2+} (3d^9) - \text{O} - \text{Cu}^{2+} (3d^9)
\]

Anderson 1961

\[
\frac{2Z_{pd}}{\Delta^2} \left[ \frac{1}{U} \right] \rightarrow \frac{2Z_{\text{eff}}}{U}
\]

New term

\[
\frac{2Z_{pd}}{\Delta^2} \left[ \frac{2}{2\Delta + U_{pp}} \right] \rightarrow \frac{2Z_{\text{eff}}}{U_{\text{eff}}}
\]

Anti ferro magnetic

For High \( T_c \) \( J_s \approx 0.18 \text{eV} \)
leaves behind in the intermediate state $2p^4 S=1$ (Hunds rule).
For an antiferro $2p^4 S=0$ higher in energy by about 1 eV $J_H$(Oxygen)

\[ J = 2\Sigma_{p_{de}}^{4} \left[ \frac{2}{2\Delta} - \frac{2}{2\Delta - J_H(\text{oxygen})} \right] \]

This is a small ferro exchange

\[ J(\theta) = J_{AF}(180^\circ) \cos^2 \theta + J_{F}(90^\circ) \sin^2 \theta \]
Exchange for $\text{Teg}$ unpaired spins

$$J_{\text{an}T_i} = \frac{2 J_{\text{pd} T_i}^4}{\Delta^2} \left[ \frac{2}{2\Delta + U_{pp}} + \frac{1}{U_{dd}} \right]$$

by rotating one bond about an axis $\perp$ to the bond out of the page $T$ does not change but for rotation in the page it is like eg orbitals

$I(I_{Teg}) \sim \frac{1}{8} I(\text{eg})$ for same angle
i.e $I_{\text{pd} T_i} \sim \frac{1}{2} I_{\text{pd} \pi}$
\[ t_{ij} = t \cos \left( \frac{O_{ij}}{2} \right) \]

\[ O_{ij} = \text{angle between neighbouring spins} \]
IF We have Spectator Spins

\[ \text{Mn}^{3+} \quad \text{d}^4 \]

\[ \begin{align*}
3x^2 - r^2 & \quad 3y^2 - r^2 \\
J_{\text{ferro}} & = -2 \left[ \frac{2t_2^2}{U - J_H} - \frac{2t_2^2}{U + 3J_H} \right] + \frac{2(\delta/3)^2}{U} \\
& = -\frac{2t_2^2}{U} \left[ \frac{4J_H}{U} - \frac{1}{3} \right] \text{ anti-ferro}
\end{align*} \]

**FM**

- 3d
- Ligand 2p
- unfilled orbital orthogonal to filled orbital
- FM-coupled metal spins
- 3d + 3d vacant
Example Cu$^{2+}$ as in LaCuO$_4$  \((d^9 \text{ s}=1/2)\)

For the N-1 electron states we need $d^8$, $d^9L$, $d^{10}L^2$ where $L$ denotes a hole in O 2p band. The $d^8$ states exhibit multiplets...
To calculate the PES spectrum

- Consider a Cu 2+ impurity in a O Lattice
- The ground state and optical spectrum will be given by the one hole Greens function
- The PES spectrum will be given by the two hole Greens function which also includes the lowest energy electron removal state of the various possible symmetries and spins.
Anderson Impurity calculation

Note the large Energy scale Covered by each State!!

Zhang Rice singlet

\[
\text{Ground state: } (\sqrt{0.7} d^9 + \sqrt{0.3} d^{10}) \rightarrow 68\% d^{10} (Cu^{2+}) \\
24\% d^{11} (Cu^{1+}) \\
8\% d^{12} (Cu^{1+})
\]
High Spin → Low Spin

Multiple Charged Impurity States
Resonant Photoemission spectrum of CuO

Energy below Ef in eV
Zhang Rice singlets
Cannot be represented
By single Slater determinant

\[ \psi_i(x^2-y^2) = \frac{1}{\sqrt{\pi}} \left[ -p_{2x} + p_{2y} + p_{3x} - p_{4y} \right] \]

\[ T_{2d}(e_1) = 2 T_{2d} \text{ (single bond)} \]

Singlet stabilized by \[ \frac{J - \chi[2T_{2d}]}{\Delta_{CT}} \]
Example of two cluster calculations to obtain the parameters
For a low energy theory (single band Hubbard or tJ)

\[
\begin{align*}
E &= 0.4 \\
\delta &= 0.17
\end{align*}
\] 2,5 model

Band width for \( t = 0.4 \) = 3.2 eV
Eskes et al. PRB
44,9656, (1991)

0 to 1 hole spectrum
One of the Cu’s is d9
The other d10 in the
Final state. Bonding
Antibonding splitting
Measure d-d hoping

1 hole to 2 holes final
State is od9 on both
Cu’s Triplet singlet
Splitting yields super
Exchange J

2 holes to 3 holes final
state is d9 for both Cu’s
Plus a hole on O forming
A singlet (ZR) with one of
The Cu’s. Splitting in red
Yields the ZR-ZR hoping
integral as in tJ
Orbital degeneracy

\[ \sigma^\prime (l_y^3 s_y^4) \quad d^6 (l_y^7 s_y^1) ; \quad d^4 d^4 d^4 (l_y^9 s_y^1) \]

\( \rightarrow \) Strong JT ion \( \rightarrow \) Weak JT

How can we lift degeneracy

1) JT distortion \( \rightarrow \) Lower symmetry
   \[ \text{Cu}^2+ (d^9) (l_y^6 s_y^1) \quad O_\infty \rightarrow O_{4d} \]

2) Spin orbit (For \( l_y^7 \))
   \( \Delta \approx 30 \text{ meV} \) for 3d TIT's \( \text{La}_2 \text{Sr}_2 \text{CoO}_4 \)
   \( \Delta \approx 300 \text{ meV} \) for 4d TIT's \( \text{Peltinger} \)

\( \rightarrow \)

3) Orbital ordering
4) Charge disproportionation
Orbital Degeneracy

Free ion \[ d_{\text{5s}} \]

\[ \downarrow^{2} \quad e_{g}^{2} \]

\[ 102 \text{eV} \]

\[ \downarrow^{3} \quad t_{2g}^{3} \]

\[ \text{On} \]

\[ \text{distorted} \]

\[ \text{S-Orbital} \sim 0.05 \text{eV} (\epsilon_{\text{eq}}) \]

\[ \text{Strong } U \text{ and } J_{N}(\sim 0.8 \text{eV}) \]

\[ \text{Fe}^{4+}, \text{Mn}^{3+}, (d^{4}) \]

\[ \text{Ni}^{2+}, \text{Cr}^{3+}, \text{V}^{2+} \]

\[ \text{Cr}^{3+}, \text{V}^{3+}, \text{Ti}^{4+} \]

\[ \sim Q \text{S}^{-1} \]
Orbital Ordering

Spin waves vs. Orbital Waves?

\[ H = \sum \frac{1}{2} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum \frac{1}{2} D_{ij} \mathbf{Q}_i \cdot \mathbf{Q}_j + \sum \frac{1}{2} \mathbf{D} \cdot \mathbf{D} \cdot \mathbf{Q}_i \cdot \mathbf{Q}_j \]

in general \( \mathbf{Q} \) very complicated

(See Ishihara, Inoue, Maekawa for Mn pervoskites)

Orbitons

modified magnon E(k)

perhaps even 2 part bound states [Orbilon-Magnon]

\[ \downarrow \]

Magiton \leftrightarrow Orbilon

Vanden Brink et al. (1998)
In ab ferro. Spin coupling antiferro. Orbital Coupling Along c visa versa
Orbital Degrees of Freedom

Ferromagnetic and AFM Mott Insulators

3d-Orbitals

Orbital Excitations fundamentally originate from \textit{dd} excitations

Orbital Order

Orbital Excitations/”Orbitons”

Maekawa et.al. (2001)

LiVO$_2$ V(d$^2$—S=1)
Two electrons in a t$_2$g Orbital

Rock salt structure
Alternateing V Li O layers
Each have a triangular lattice
All signs of magnetic dips

\( (T - B) \)\n
\( G_2/600K \)
This orbital ordering yields a large internal Antiferromagnetic exchange and a weak external ferromagnetic exchange.

Orbital ordering removes frustration

Pen et al PRL 78,1323
\[ \mathcal{H} = \frac{J}{2} \sum_{i,j} S_i \cdot S_j \quad (\text{All bonds eq}) \]

\[ S^2 = (\hat{S}_1 + \hat{S}_2 + \hat{S}_3)^2 = 3 S^2 + \sum_{i,j} S_i \cdot S_j \]

\[ \sum_{i,j} S_i \cdot S_j = S^2 - 3 S^2 \]

\[ = S(S+1) - 3S(S+1) \]

\[ S = 0, 1, 2, 3 \]

\[ \sum_{i,j} S_i \cdot S_j = -6 \quad (S=0) \]

\[ -4 \quad (S=1) \]

\[ 0 \quad (S=2) \]
Result of orbital ordering is a lattice of spin zero triangles. The coupling between triangles is weakly ferromagnetic.
YVO3 Pervoskite structure  
V(3+) 2 electrons in T2g Orbitals S=1.  
Note the tilted and Rotated octahedra. Results in a Staggered magnetic anisotropy And this breaks the inversion Symmetry at O sites and allows For DM coupling and canted antiferromagnets

\[ \vec{D} \cdot \vec{S}_1 \times \vec{S}_2 \]

Tsvetkov et al  
PRB 69, 075110 (2004)
YVO₃ Perovskite
V(d² S=1) O not In inversion symmetry DM canting competing With staggered magnetic Anisotropy. See Aharoni’s lectures
All V have one electron in a dxy orbital

O between the V ions are not in inversion center
Tilted Octahedra  D.SxS interactions  compete
With local staggered anisotropy